

Vesicular Carbon In Strongly Heated IDPs

D. E. Brownlee¹, D. Joswiak¹, and J. P. Bradley², ¹Dept. of Astronomy, University of Washington, Seattle, WA 98195
²MVA Inc. Norcross GA 30093, and School of Matl. Science and Engr., Georgia Inst. of Technology, Atlanta, Ga 30332.

The carbon content of typical 10 μ m IDPs is several times higher than bulk CI abundances [1]. The carbon-rich particles are important because they may be samples of carbon-rich outer solar system materials such as comets and P and D asteroids. The C content is so high in many IDPs, that abundant carbon is directly observable with the TEM in microtome sections. Carbon occurs as fine matrix-like material between grains and as thin coatings on grains [2] but its most conspicuous occurrence is as "bulk" amorphous carbon regions that range in dimensions up to micron-size. In some cases this bulk carbonaceous material is vesicular with rounded voids of 10nm to micron size. In very extreme cases, some IDPs are just porous frameworks consisting of interconnected bubbles. A good example is the IDP section in Thomas et al. [1] that was measured to be 90% carbonaceous material by volume. In vesicular carbon it appears that carbonaceous matter has undergone plastic deformation. The vesicles could form by processes related to the original formation of IDP parent bodies or even interactions with ice, but a likely formation mode is that they are the result of atmospheric entry heating. Typical 10 μ m unmelted IDPs are heated in the range of 400°C to 1200°C for a few seconds during entry. This heat pulse will alter abundant organic matter in IDPs and it may lead to vesicle formation.

Although the bulk of carbonaceous matter in IDPs has not been studied in detail, it is likely that it is similar to the insoluble macromolecular carbon [3] in CI's. This kerogen-like material has an approximate composition of C₁₀₀H₄₈N_{1.8}S₂O₁₂ [4]. Atmospheric heating of this aromatic-rich material should result in carbonization in a manner similar to the industrial formation of coke from coal or carbon fibers from polymeric precursors. At 300-400°C coal becomes plastic [6] and further heating drives off other elements leaving a final product that is rigid and nearly pure carbon. In IDPs, heating above 300°C may yield a period of thermoplastic behavior of carbonaceous components where vesicles grow due to the release of volatiles. The volatiles lost during pyrolysis could include H₂, H₂O and CO as well as heavier molecules such as benzene and toluene. Further heating to temperatures of 1000°C and above would yield a rigid carbonized product with possibly little memory of its original composition. Mobilization of macromolecular carbon in the initial stages of heating will lead to redistribution of carbon.

To investigate thermal effects on carbon we examined IDPs that were strongly heated during atmospheric entry as well as IDPs that were artificially heated in the microprobe and SEM. The naturally heated IDPs were of two types; particles that were quantitatively shown to be strongly heated by the Nier/Schlutter He release technique [6] and metal-mound-silicate (MMS) IDPs that underwent obvious

partial melting during atmospheric entry. The MMS particles are rare IDPs [7] that consist of three immiscible components: silicate spherules, FeNi metal mounds and irregular lacy clumps of carbon-rich matter. Often these components are bound as weakly consolidated cluster particles. The artificially heated IDPs were heated to solidus temperatures by electron beam heating and the final product is very similar to MMS particles. Stratospheric IDPs were placed on alumina disks and heated with a focused 20KV beam. Poor thermal contact with the alumina substrate permits particle temperatures >1200°C with microamp currents.

We found many interesting phenomena in the strongly heated particles. Most of the samples do contain vesicular carbon and this strongly supports the hypothesis that the vesicles are the result of thermal processes. This shows that vesicle formation in IDP carbon does occur during atmospheric heating but it does not prove that this is the primary origin of typical vesicular carbon in IDPs. Unfortunately we do not have any IDPs that have not been heated during entry. It is likely that vesicle formation occurs at temperatures of only a few 100°C and that all collected IDPs have thermally produced vesicular carbon.

In the MMS particles and the electron beam heated particles that were heated above 1000 °C, we observed very interesting processes that relate to processing of carbon in IDPs. The results also provide insight into a new method of providing at least part of the siderophile depletion seen in chondrules and cosmic spherules. We find that the most strongly heated particles are composed of largely melted silicates plus metal mounds and lacy chunks of carbon, the most refractory IDP component and the only one not affected by melting. The data suggest the following processes. Initial moderate heating partly mobilizes carbon and produces vesicle formation. Continued heating carbonizes the organic fraction as silicate components begin to melt. Silicate melt formation is accompanied by reduction to form metal. Metal formation may be partly due to implanted hydrogen but carbon clearly plays a major role in the reduction process. The carbon components are filled with 10nm and larger rounded metal grains that contain chondritic Ni/Fe ratios and Cr contents up to several weight percent. In some particles the metal beads are surrounded by 10nm layers of graphite whose formation appears to have been catalyzed by the metal beads. In some regions, graphitic tube-like structures are seen with metal beads at the ends.

This work provides several new insights. The thermal carbonization of IDP polymeric material must involve mass loss and bulk carbon abundances measured for IDPs should be considered lower limits. Carbonaceous material undergoes plastic deformation during atmospheric entry and

Vesicular carbon in IDPs: D. E. Brownlee, D. Joswiak, and J. P. Bradley

textural relationships between carbon and other IDP components are likely to be altered in the process. Graphite does exist in IDPs but it appears to have been produced during entry heating and it is only observed in particles heated $>1000^{\circ}\text{C}$. Rapid melting of carbon-rich chondrule and cosmic spherule precursors can lead to formation of a carbonized component that contains small metal beads. In melted particles the carbon-metal bead component is immiscible and is likely to separate from the silicate fraction depleting its siderophiles. This process may play a role in depletion of siderophiles from chondrules and in depleting siderophiles and Cr from cosmic spherules. The formation of carbon with included metal beads explains a mysterious Fe-Si component previously seen in automated point count EDX analyses of IDP microtome sections. In some cases this must be pyrolyzed carbon with tiny embedded metal beads. The Si component is likely to be residual silicone oil (used during collection) trapped in highly porous carbon. In some cases the carbonized matter with imbedded 10nm metal beads is texturally very similar to GEMS [8]. It is likely, in some cases, that these have been previously confused with true carbon-free GEMS composed of glass with metal and sulfide beads. Published mention of carbon dominated GEMS-like components may just be thermally altered carbonaceous matter containing metal grains. The thermal degradation of carbonaceous matter in IDPs is an important process and development of techniques for its quantitative measurement could lead to a good heating index for IDPs and provide a means of identifying particles that have suffered minimal atmospheric entry heating. Comet samples to be returned by the STARDUST Discovery mission will also be heated during collection and a full understanding of these alteration processes will be important to distinguish original properties from thermal alteration effects.

References [1] Thomas, K., L. (1994) in *Analysis of Interplanetary Dust*, AIP Conf Proc 310, 165-172. [2] Keller, L. P., Thomas, K. L. and McKay, D. S. (1996) *LPSC 27*, 659. [3] Cronin J. R., Pizzarello, S., and Cruikshank, D. P. (1988) in *Meteorites and the Early Solar System*, U. Arizona Press, 819-857. [4] Zinner, E. (1988) in *Meteorites and the Early Solar System*, U. Arizona Press, 956-983. [5] Porter, H. C. (1924) *Coal Carbonization*, Amer. Chem. Soc Monograph. 442 pp. [6] Nier, A. O. (1994) in *Analysis of Interplanetary Dust*, AIP Conf Proc. 310, 115-126 [7] Brownlee, D. E., Olszewski, E. O. and Wheelock, M. W. (1982) *LPSC 13*, 71 [8] Bradley J. P. (1994) *Science* 265, 92.

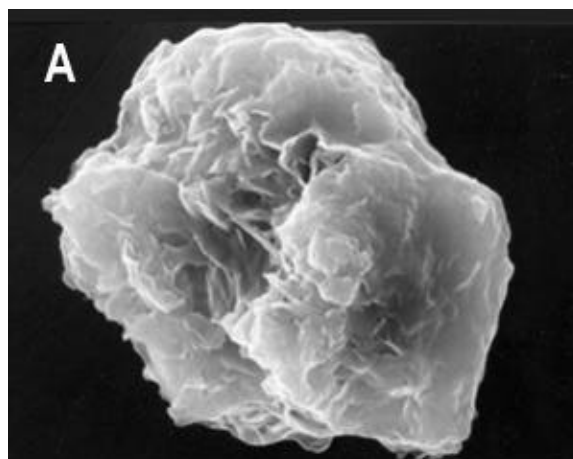


Fig. 1 Original IDP before laboratory heating.

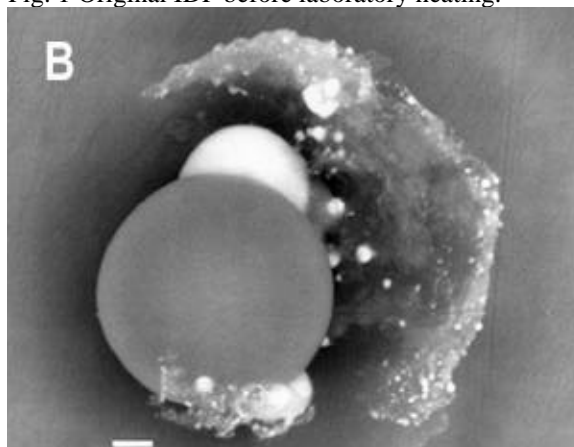


Fig 2 Particle above after electron beam heating. The grey sphere is silicate, the bright beads are FeNi metal and the whispy unmelted material on the right is carbon, standing as high as the sphere. Scale bar-1 μm .

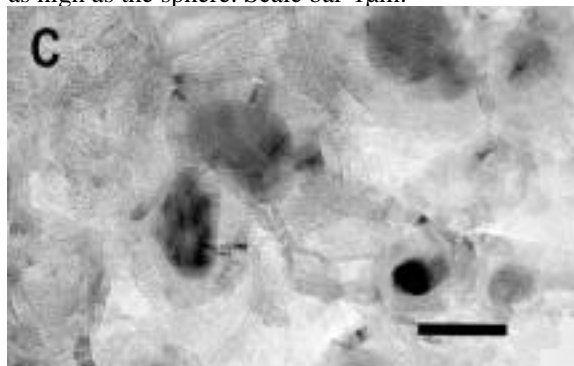


Fig. 3 A microtome slice of a natural Metal Mound Silicate IDP, showing porous carbon and kamacite with 10nm graphite rims. Scale bar-20nm.